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Collisional Behaviour with Ar of the Λ Doublets of CH(X $^2\Pi$) $N'' = 15$ produced in the Two-photon Dissociation of CH_2CO at 279.3 nm

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Relaxation of the $N'' = 15$ Λ doublets of CH(X $^2\Pi$) produced in the two-photon dissociation of ketene at 279.3 nm has been observed in the presence of Ar. An initially equilibrated nascent Λ doublet population is seen to be removed in such a way that the component of A″ symmetry (π orbital perpendicular to the plane of rotation) dominates. The application of recent theory describing collisions of $^2\Pi$ diatomics with closed shell atoms is briefly discussed.

The CH radical is one of the most ubiquitous and reactive of all free radicals and plays a key role in the chemistry of combustion and atmospheric systems. In addition to its kinetic importance in elementary reaction steps, CH is of fundamental interest to theoreticians and experimentalists studying the dynamics of collisional quenching and energy transfer processes of small radical species. In particular, state-resolved observations of the population of the Λ doublets of the radical yields valuable information on the stereochemical behaviour of the singly occupied π electron orbital with respect to the rotating molecular framework.

An initial bias towards population in specific Λ doublets has been noted in the dispersed emission of nascent rotational levels in the first excited electronic state of CH($^2\Delta$), a commonly observed product from the multiphoton dissociation of CH containing polyatomics. For example, Stuhl and co-workers[1] have observed a propensity for population of CH($^2\Delta$) in rotational levels of Π(A′) symmetry (pπ orbital parallel to the diatomic rotating plane) following the 193 nm photolysis of acetone. This is in partial agreement with Nagata *et al.*[2] for the same system who report a switching to Π(A″) propensity for rotational levels greater than $N' \approx 20$. Similar experiments with ketene, CH_2CO, as a precursor at a photolysis wavelength of 193 nm, also report a higher intensity emission in the symmetric Λ component for rotational levels with $N' = 14$–19, but the opposite for levels $N' = 20$–23.[3]

The present work focuses on the Λ doublet populations of the ground electronic state. We have recently reported measurements on the nascent rotational populations for ground-state CH(X $^2\Pi$) produced from the two-photon photolysis of ketene at wavelengths of 279.3 and 308 nm.[4] At 279.3 nm the nascent rotational distribution probed by LIF exhibits equal population in the Λ doublets, while at 308 nm there was a slight degree of orbital alignment in favour of Π(A′) symmetry for the higher rotational levels populated. The likely dissociation pathways leading to these results were discussed. Here we report on the subsequent evolution of the CH(X $^2\Pi$) rotational populations in collisions with Ar. We observe a significant inequality in the initial behaviour of the populations of the two Λ symmetries with respect to both time and pressure of Ar. These observations must indicate a preferential rotational energy transfer mechanism, dependent on π orbital symmetry, that operates for certain rotational levels of CH in collisions with the inert gas. The results are discussed in terms of the extensive theoretical treatment for inelastic scattering of $^2\Pi$ diatomics which has been developed by Alexander and co-workers.[5–8]

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Experimental

In these experiments a standard LIF detection apparatus was used which has been described in more detail elsewhere.[4,9] The CH(X $^2\Pi$) radical was generated by the two-photon photolysis of ketene, CH_2CO, at 279.3 nm,[4] and detected by on-resonance LIF within the Q and R branches of the CH A $^2\Delta$–X $^2\Pi$ system at wavelengths between *ca.* 418 nm and 432 nm.[10] Plane polarised photolysis light at 279.3 nm was produced using the frequency-doubled output of a Quanta Ray 5200 dye laser pumped by a XeCl Questek 2240 excimer. The probe laser radiation was obtained either from a Molectron Corp. UV 24 nitrogen laser pumped Molectron DL 200 dye laser (energies up to *ca.* 50 μJ pulse^{-1}, bandwidth *ca.* 1.0 cm^{-1}) or a Lambda Physik excimer laser pumped dye laser, EMG101/FL2002 combination (output up to 10 mJ pulse^{-1} and bandwidth of *ca.* 0.4 cm^{-1}). The LIF was observed perpendicular to the orthogonal intersection of the horizontal photolysis and probe laser beams using an EMI 9813QKB photomultiplier tube and an appropriate interference filter. Data were acquired either by gating and integrating the signal using a Brookdeal 9415/9425 boxcar combination and a chart recorder or by digitisation *via* a 20 MHz Thurlby DSA524 Digital Storage Adaptor and a PC.

Ketene precursor was prepared as described previously by the pyrolysis of acetone vapour in He passed over an electrically heated nichrome element at *ca.* 650 °C.[11] Purity was always checked by mass spectrometry and UV absorption between 200 and 400 nm. When not frozen the ketene was stored at pressures less than 20 Torr in a darkened bulb to prevent polymerisation. Argon (Ar) diluent was obtained from BOC with a stated purity of 99.995% and used as received. Experiments were conducted using a static gas sample within the stainless steel cell of *ca.* 30 mTorr CH_2CO and variable partial pressures of Ar bath gas.

Each rotational level within the CH(X $^2\Pi$) and CH(A $^2\Delta$) manifolds is split by spin–orbit coupling [Hund's case (b)] and by Λ doubling, although the magnitude of the splitting is considerably greater in both instances for the ground state. The selection rules allow transitions within the A–X system from all four levels associated with a given lower state rotational quantum number N''.[12] The fine-structure populations can therefore be obtained directly from a LIF scan within a single rotational branch. For CH(X $^2\Pi$) with its relatively large rotational constant ($B_e = 14.46$ cm^{-1} [13]) but weak spin–orbit coupling constant ($A = 28.14$ cm^{-1} [10]), the Λ splitting rapidly dominates the spin–orbit splitting as rotational energy increases. The bandwidth of the Molectron laser as probe was sufficient to resolve the Λ doublets but not the spin–orbit components contained within each. In order to standardise the notation associated with the rotational levels

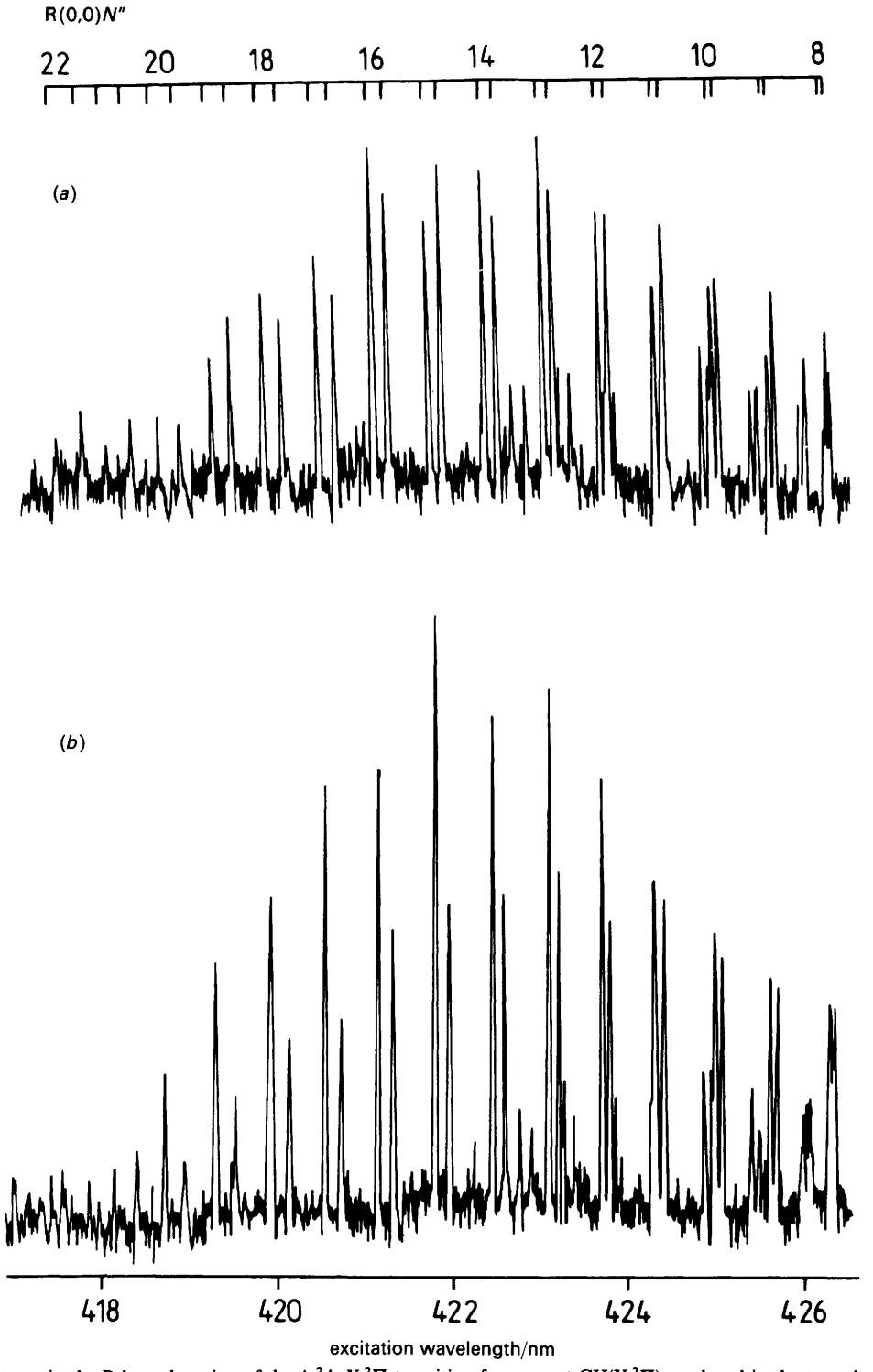

Fig. 1 (*a*) LIF spectrum in the R branch region of the $A\,^2\Delta$–$X\,^2\Pi$ transition for nascent $CH(X\,^2\Pi)$ produced in the two-photon dissociation of ketene at 279.3 nm using the Molectron nitrogen laser pumped dye laser combination as probe. Positions of the R branch transitions in the (0,0) band are indicated as a function of N''. For each N'' doublet the transition at lower wavelength probes the levels of $\Pi(A'')$ symmetry, whilst that at higher wavelength probes the levels of $\Pi(A')$ symmetry. Partial pressure of ketene 30 mTorr. (*b*) As for Fig. 1(*a*), but under collisional conditions of 5 Torr pressure of Ar and a photolysis-probe delay of 0.3 μs (equivalent to *ca.* 15 gas kinetic collisions). The preferential population of $\Pi(A'')$ levels under collisional conditions is clearly seen for N'' levels $\geqslant 12$.

of such systems Brown *et al.*[12] and Alexander *et al.*[14] have classified the fine-structure levels according to the behaviour of the electronic wavefunction on reflection in the plane of rotation of the diatomic in the limit of high J. As the case (b) limit is approached the F_{1e} and F_{2f} wavefunctions of a $^2\Pi$ state acquire symmetric character with respect to this reflection and are denoted $\Pi(A')$ while the F_{1f} and F_{2e} wavefunctions acquire antisymmetric character and are denoted $\Pi(A'')$. These correspond to the singly occupied π orbital of the radical being aligned parallel or perpendicular to the plane of rotation, respectively. For the $N'' = 15$ levels of $CH(X\,^2\Pi)$, the subject of the present study, the R branch transition consists of a doublet, the higher wavelength component of which corresponds to transitions from the unresolved F_{1e} and F_{2f} levels, each of $\Pi(A')$ symmetry, with the lower wavelength component being from F_{1f} and F_{2e} levels, both of $\Pi(A'')$ sym-

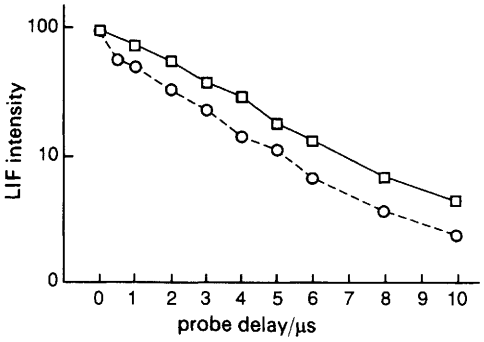

Fig. 2 Semi-logarithmic plot of the population of both components of the $N'' = 15$ Λ doublet of CH($X\,^2\Pi$) as a function of increasing time delay following photolysis at 279.3 nm. Partial pressures of CH_2CO and Ar were 30 mTorr and 1.0 Torr, respectively. The squares correspond to CH rotational levels of Π(A″) symmetry and the circles to levels of Π(A′) symmetry.

metry. This part of the spectrum thus gives a convenient probe of the Λ doublet behaviour.

Two distinct pump–probe beam relative polarisation geometries could be investigated, either both electric vectors parallel to each other and vertically orientated with respect to the laboratory frame or alternatively with the polarisation of the photolysis beam rotated through 90°. At short pump–probe delays copious amounts of nascent 'background' emission from excited CH($A\,^2\Delta$) had to be subtracted from the LIF signal of interest and significantly impaired sensitivity.

Results

Previous work in this laboratory has shown that the nascent population of CH prepared by the two-photon photolysis of ketene at 279.3 nm clearly has a 1 : 1 ratio in Λ doublet population for all N'' levels probed in the R branch region between 418 and 426 nm.[4] The LIF spectrum is reproduced here in Fig. 1(*a*) for comparison. The corresponding spectrum of CH under collisional conditions (5 Torr Ar at a delay of 0.3 μs, corresponding to *ca.* 15 gas kinetic collisions) is illustrated in Fig. 1(*b*). Here there are obvious unequal Λ doublet intensities for all rotational levels $N'' \geqslant 12$.

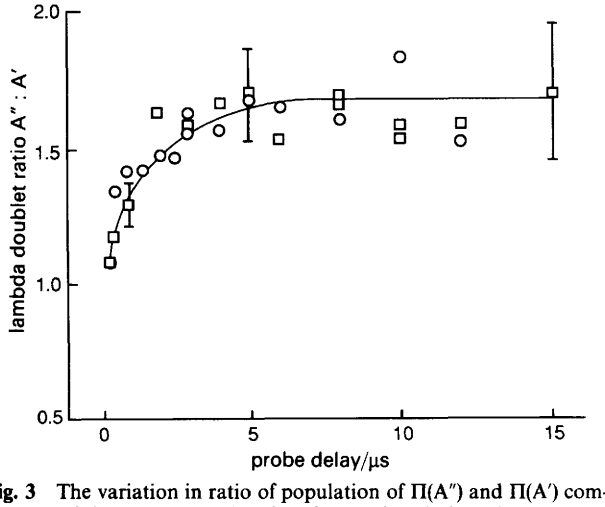

Fig. 3 The variation in ratio of population of Π(A″) and Π(A′) components of the $N'' = 15$ Λ doublet of CH (photolysis at 279.3 nm) as a function of probe delay at a fixed Ar pressure of 0.5 Torr. The circles correspond to both photolysis and probe laser beams vertically plane polarised with respect to the laboratory frame, and the squares to a 90° relative polarisation geometry. The Π(A″) : Π(A′) ratio rises to a limiting value in a way that is independent of polarisation geometry. The increasing error bars with time reflect the reduction in the magnitudes of the absolute LIF signals as CH is removed.

For this effect to be attributed to unequal Λ doublet populations in the ground $^2\Pi$ state, the influence of different excitation and fluorescence rates needs to be considered. First, lifetimes τ of the $^2\Delta$ $N' = 16$ levels accessed in the transition were found to be represented by $\tau = 560 \pm 40$ ns for Ar pressures between 0 and 5 Torr, in agreement with previous measurements[15–18] and eliminating the effect of quenching of the upper $^2\Delta$ level on the fluorescence intensities. Secondly, the Λ doublet ratio was found to be independent of relative polarisation of the pump and probe beams, showing that alignment effects were negligible. Finally, the ratio remained constant over a ten-fold change in probe laser intensity, eliminating saturation effects in the transition. The propensity is thus a phenomenon occurring within the ground state of CH, with the propensity for the shorter wavelength component of the transition for a given N'' indicating a greater population for CH of Π(A″) symmetry.

From Fig. 1 it can be seen that although disequilibrium between the Λ doublet levels has been established in a time corresponding to *ca.* 15 gas kinetic collisions, the overall rotational state population is not markedly affected, *i.e.* the two rotational distributions for Fig. 1(*a*) and (*b*) peak at approximately the same value of N''. It should also be noted that the disequilibrium effect is most apparent at high N''. Rotational levels with $N'' \leqslant 12$ appear to be unaffected under the collisional conditions.

Fig. 2 shows the time dependence of the two Λ doublets in the presence of Ar. Both components decrease monotonically with time, but it can be seen that a disequilibrium between the two is established rapidly (< 1 μs for a pressure of 1 Torr Ar as shown in Fig. 2) and is maintained over a timescale of several lower state lifetimes. Fig. 3 shows the evolution of the Λ doublet ratio as a function of time at a pressure of 0.5 Torr Ar and 30 mTorr ketene, reaching a limiting value of *ca.* 1.7 in a timescale corresponding to *ca.* 20 Ar collisions. Under these conditions, CH($X\,^2\Pi$) is removed predominantly by reaction with ketene,[9] but the effect was shown to be dependent on the presence of Ar by experiments in which the Λ doublet ratio was found to be invariant (1.1 ± 0.1) over the same timescale with ketene alone, and to show a similar increase to a limiting value when measured as a function of Ar pressure at constant time delay and ketene pressure.

Our conclusions about the anomalous behaviour are as follows: (1) The relaxation of a 'hot' distribution of CH rotational states initially in Λ doublet equilibrium in collisions with Ar (when chemical removal by reaction with ketene also occurs) takes place through a marked Λ doublet disequilibrium. (2) The effect is not solely due to preferential chemical removal of a single Λ doublet; Ar collisions are necessary. (3) The persistence of the disequilibrium after the photolysis pulse is over shows that the effect is not dominated by collisional processes affecting the initial Λ doublet population. In previous studies it was proposed that the ketene dissociation process involved single-photon absorption to a predissociative state followed by a second absorption step.[4] Any collisional relaxation of the intermediate to a lower-energy longer-lived state might affect the subsequent energy distribution (and possibly the Λ doublet ratio). A collisional effect on the nascent CH quantum yield was seen, but as Fig. 2 and 3 show, the disequilibrium effect persists at timescales orders of magnitude greater than the duration of the photolysis pulse.

Discussion

We first note that the ketene system is not the first in which such anomalous Λ doublet ratios have been seen. In an experiment very similar to this, Stuhl and Heinrich[1] have

observed an almost identical effect on the $N'' = 15$ Λ doublets of CH found in the multiphoton dissociation of CH_2Br_2 at 193 nm. An initially equal ratio of Λ doublets increased to a Π(A″) : Π(A′) ratio value of *ca.* 2.5 with Ar collisions, *i.e.* with both time and pressure of inert diluent. The collisional behaviour described in the present work is a quenching for CH incorporating a preference for Λ doublets of Π(A″) symmetry, regardless of the nascent population of Λ doublets that has been produced on photolysis. This bias is for the electron density of the π^1 electron to lie parallel to the total angular momentum vector ***J***, and perpendicular to the plane of rotation of the radical, in the limit of high angular momentum.[14]

Macdonald and Liu[19] have used a cross molecular beam apparatus to collide CH $N = 1$ radicals with He atoms at collision energies up to 12 kJ mol^{-1}. An initially equal distribution of all four fine-structure states of $N = 1$ resulted in preferential rotational energy transfer of population to the 1f and 2e states [of Π(A″) symmetry] in levels of $N > 1$, as compared to population in the 1e and 2f states of the same final levels. Towards the upper end of collision energies, the ratio of the population of the two symmetries of CH in the excited rotational levels was typically Π(A″) : Π(A′) = 2.5 : 1. The ratio increased exponentially with decreasing energy as the threshold for the excitation process was approached. The probe-laser resolution available to us in the present work was insufficient for such full characterisation of all fine-structure states. We are also concerned wth rotational quenching of the CH radical in downward transitions, rather than the measurement of differential cross-sections for net inelastic energy transfer to the radical in upward rotational transitions.

Theoretical work on a general formalism for inelastic scattering of a diatomic radical with a structureless collision partner has been extensively developed by Alexander and coworkers.[5,6,8,20] In these open-shell systems the nearly degenerate potential-energy surfaces at long range may interfere as a collision partner approaches, and prevent treatment of the collision as an event taking place on a single surface. Complications arise also from different coupling systems of the various momenta. Calculations have been applied to the specific example of inelastic scattering and resultant orbital alignment of CH in collisions with He,[8] and general agreement found with the molecular beam results.[19] The nonstatistical population of the final state Λ doublet levels arises directly from an interference between the scattering amplitudes on the two potential-energy surfaces upon which inelastic collisions occur. Approach of a spherical scattering partner to the $^2\Pi$ radical lifts the electronic degeneracy of the $^2\Pi$ state giving a total wavefunction for the system that is either symmetric A′ or antisymmetric A″ with respect to reflection of the electronic spatial coordinates in the triatomic plane. Collisions are described using average and difference linear combinations of these surfaces, $\frac{1}{2}(V_{A'} + V_{A''})$ and $\frac{1}{2}(V_{A''} - V_{A'})$, respectively. In a Hund's case (b) diatomic, where neither ***L*** nor ***S*** is strongly coupled to the internuclear axis, both the average and difference potentials can contribute to both fine-structure conserving collisions (influence of the average potential) and fine-structure changing collisions (influence of the difference potential). Interference between the scattering amplitudes of the different paths which lead to the same final spin–orbit state imposes a bias in differential cross-section and a propensity in Λ doublet population. The preferred final symmetry is dependent on the relative signs and magnitudes of the average and difference potentials.

A single theoretical calculation for loss of rotational energy in the CH + He system, $J = \frac{3}{2}$, $F_1 \rightarrow J = \frac{1}{2}$, F_2, predicts a differential cross-section ratio of $\sigma_{A''}/\sigma_{A'} = 0.53$,[8] *i.e.* preferential de-excitation into states of Π(A′) symmetry. This prediction has not been tested experimentally and is opposite to our findings presented here. The reason for the discrepancy presumably arises from the different functional form of the potential-energy surfaces required to describe collisions of CH with a much higher degree of rotational excitation and with a heavier Ar scattering partner as investigated in the present work. A change in relative signs of the average and difference potentials will affect the symmetry of the states [to Π(A″) for de-excitation collisions] of a particular level into which CH is preferentially quenched. The long-range dispersion interaction in the collision is proportional to the polarisability of the spherical scattering partner and will be strongest when the π electron of CH lies in the orbital within the triatomic plane defined by the collision. Since the polarisability of an Ar atom is almost an order of magnitude greater than that of He, the signs of the dispersion interaction for the two symmetries may play an influential role in the overall balance of scattering amplitudes.

A further consideration is that the entire scattering process may be a J (or N) dependent quantity. This would account for the observed discrepancy that Λ doublets with $N'' > 12$ in the LIF spectrum under collisional conditions for CH produced at 279.3 nm photolysis show a collisional propensity while levels of lower rotation continue to exhibit the nascent equilibrium population [Fig. 1(*b*)]. Alternatively, this observation may be a manifestation of the system striving towards the equilibrium that would be eventually attained in all thermally populated levels at ambient conditions were it not for the population of CH being removed by chemical reaction before an equilibrium can be established.

Evidently, there is a requirement for further detailed studies on the behaviour of many more Λ doublets and specific quenching rates through individual rotational levels. In particular, fully time-resolved data for decay rates of fine structure components at fixed pressures of Ar and a thorough investigation at additional photolysis wavelengths are required to unravel completely the mechanisms underlying the dissociation pathways to, and collisional quenching of, the resulting CH fragment.

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